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TITLE: ATOMISTIC SIMULATIONS OF SURFACE RELAXATIONS IN NI, AL, AND
THEIR ORDERED ALLOYS

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ABSTRACT

We have performed a series of simulations to examine the atomistic nature of surface relaxations in pure metals and ordered alloys. The surface relaxations ($\Delta d_{n,n+1}$) are shown to be oscillatory and to decay rapidly into the bulk. The period and form of the oscillation may be determined by simple geometrical arguments. The oscillation wavelength is always of order an atomic diameter. In pure metals, the surface layer of atoms always displaces inward. However, in the ordered alloys the larger atom may displace outward. On planes composed of more than one atom types, rippling occurs.

INTRODUCTION

The atomic structure of metallic surfaces has recently received considerable attention both from experimentalists and theorists. While much of this attention has been focused on surface reconstruction, surface relaxation (change in atomic spacings but not crystal symmetry) is being studied with increasing vigor. Both low energy electron diffraction (LEED) and ion scattering techniques have been applied to the determination of the structures of relaxed surfaces in pure metals and ordered alloys. Although these techniques have been used to study surface relaxation for a number of years, only recently[1] have they become sufficiently reliable to give quantitative descriptions of atomistic structure.

Concurrent with these experimental developments were improvements in methods for describing the interactions between atoms which are suitable for simulations of free surfaces. While these advances occurred on many different fronts, we will be concerned with a variant of the embedded atom method[2]. This approach describes atomic interactions via a local density term and a pair potential term, instead of the strictly pairwise interactions typically employed in atomistic simulations. These potentials have proven to be rather reliable in describing bulk and defect properties and have recently been applied to surface reconstruction in a number of FCC materials[3,4].

In the present paper we report the results of our atomistic simulations of six different surfaces in Ni and Al, and three high symmetry surfaces in B2 NiAl (CsCl structure) and L1₂ Ni₃Al (Cu₃Au structure). These metals and alloys have received considerable experimental attention. Instead of dwelling on the degree of quantitative agreement between the experiments and simulations, however, we will be describing some of the qualitative features of surface relaxation which occur systematically over the various surfaces and alloys studied.

SIMULATION PROCEDURE

In simulating the structure of these surfaces we have employed a variant of the embedded atom method[4,5]. Since this method includes a local density term in addition to a pairwise term it is inherently of many-body character. The various terms in this potential were fit to both bulk experimental data and data on the appropriate diatomics. The details of the fitting procedure

and the resultant potentials may be found in the paper by Voter and Chen elsewhere in this volume[5].

In order to determine the surface structure we construct a truncated perfect crystal containing at least 80 atomic planes parallel to the surface. In the case of the ordered alloys where two possible surface terminations exist, the initial block of atoms was constructed such that both surface terminations existed on either end of the block. In the plane of the surface we consider only one period, but employ periodic boundary conditions to effectively simulate an infinite surface. This truncated perfect crystal was then allowed to relax by minimizing the total energy of the system with respect to all atom coordinates via a straight forward gradient technique. At the end of the gradient minimization the maximum force on any atom is less than 10^{-5} eV/nm, the surface energy varies by less than 0.01 mJ/m² per simulation step and the maximum atomic displacement does not exceed 10^{-5} nm per simulation step.

PURE METAL SURFACES

Our results on the surface structures are reported in terms of the percentage changes in interlayer spacing perpendicular to the free surface. This change is simply the strain and is indicated by the symbol $\Delta d_{n,n+1}^{\text{th}}$, where the $n,n+1$ indicates the change in the separation between the n^{th} and $(n+1)^{\text{th}}$ atomic planes. An indication of the nature of the agreement between the simulation and experiments is indicated in Table I. While our results are in reasonable agreement with the LEED results[6,7] on Al(110), the agreement with the LEED[8] and medium energy ion scattering[1] (MEIS) data on Ni(110) is off by approximately a factor of 2. Nonetheless, the main qualitative features of the experimental data are accurately reproduced. These are the layer-by-layer oscillation of the sign of the relaxation and the rapid decay of the oscillation amplitude. Based on this comparison and similar comparisons on other surfaces we conclude that the potentials employed provide an accurate qualitative description of surface relaxation and quantitative accuracy within a factor of two. Therefore we expect the simulation to be able to provide a guide for the interpretation of the experimental data. The real utility of the simulation procedure is, however, its ability to scan large number of surfaces and report the proper trends in the data.

TABLE I. Comparison of the percentage changes in the interlayer spacings (Δd) near the relaxed Al and Ni (110) surfaces.

$\Delta d_{n,n+1}^{\text{th}}$	Al(110)			Ni(110)		
	Present Work	LEED (Ref. 6)	LEED (Ref. 7)	Present Work	LEED (Ref. 8)	MEIS (Ref. 1)
$\Delta d_{1,2}$	-10.35	-8.6 \pm 0.8	-8.5 \pm 1.0	-4.87	-8.7 \pm 0.5	-9.0 \pm 1.0
$\Delta d_{2,3}$	+3.14	+5.0 \pm 1.1	+5.5 \pm 1.1	+0.57	+3.0 \pm 0.6	+3.5 \pm 1.5
$\Delta d_{3,4}$	-2.75	-1.6 \pm 1.2	+2.2 \pm 1.3	-0.86	-0.5 \pm 0.7	...
$\Delta d_{4,5}$	+1.41	+0.1 \pm 1.3	+1.6 \pm 1.6	+0.34
$\Delta d_{5,6}$	-0.61	-0.15

In order to observe such trends, we plot the surface relaxations ($\Delta d_{n,n+1}^{\text{th}}$) as a function of depth into the crystal for the (110), (210), (310), (410), (320) and (520) surfaces of Al and Ni in Fig. 1. Clearly, all of the surfaces show oscillatory, periodic relaxations. Aside from their amplitudes, the Ni and Al surface relaxations are nearly indistinguishable (slight differences are observable, especially beyond the first period in the high index surfaces). Both metals appear to have the same oscillation period, approximately independent of surface. The (110), (210), (310), and (410) surfaces all have one oscillation per period. The (320) and (520) surfaces have two oscillations per period, but still have approximately the same period.

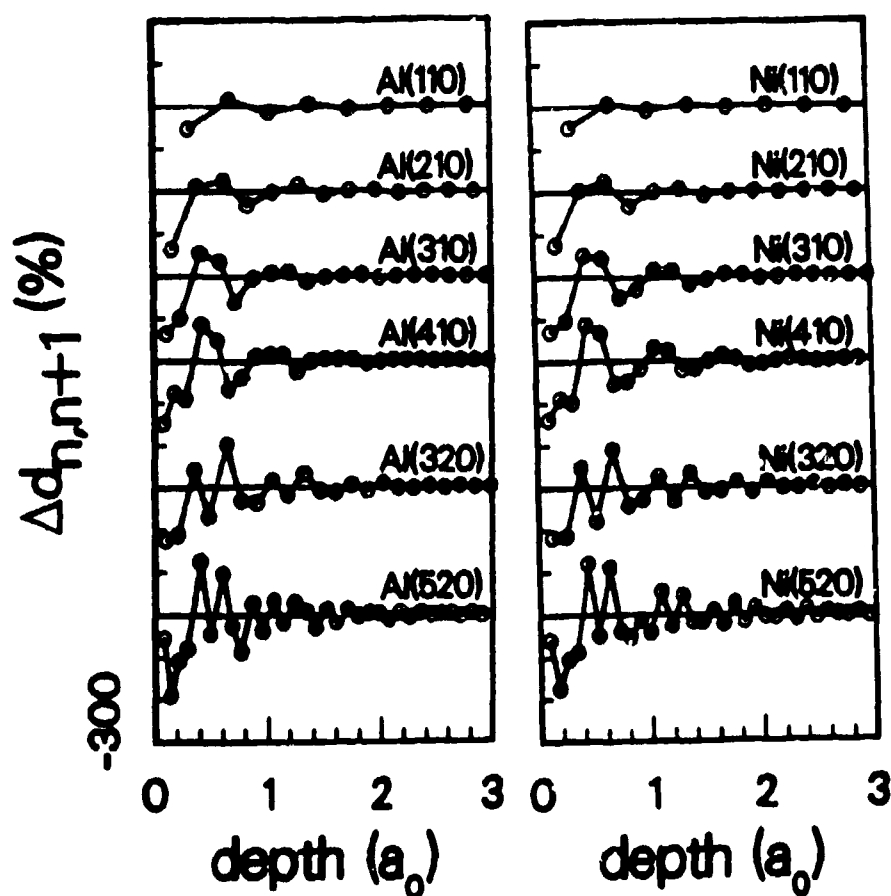


Figure 1. The surface relaxation, $\Delta d_{n,n+1}(\%)$, versus depth for 6 Al and Ni surfaces. The ticks on the vertical axis correspond to 10% each for the Al surfaces and 5% each for the Ni surfaces.

Most of these results can be understood in terms of a simple picture of surface relaxation that encompasses both the widely accepted idea of surface smoothing and steric, or hard sphere-like, interactions between atoms. In Fig. 2 we plot the position of the atoms for Ni(310) in its unrelaxed state and arrows indicating the direction and magnitude of the atom displacements upon relaxation. Clearly, the relaxation is dominated by the inward movement of the outermost atoms (labelled 1, 1', 1'') in an attempt to smooth the surface. As part of the smoothing atom 2 also moves in and atom 3 moves out. While atom 4 should move out in a surface smoothing picture it, in fact, moves in response to the inward motion of atom 1'. Atoms 1-4 (1'-4', etc.) form the first period and atoms 5-8 (5'-8', etc.) form the second period. (Note atom 5 moves in a manner similar to and in response to the motion of atom 1'; likewise, atom 7 moves like atom 3'; etc.) This period is only 2/5ths the length of the true period. Since this pseudo-periodicity may be traced to the

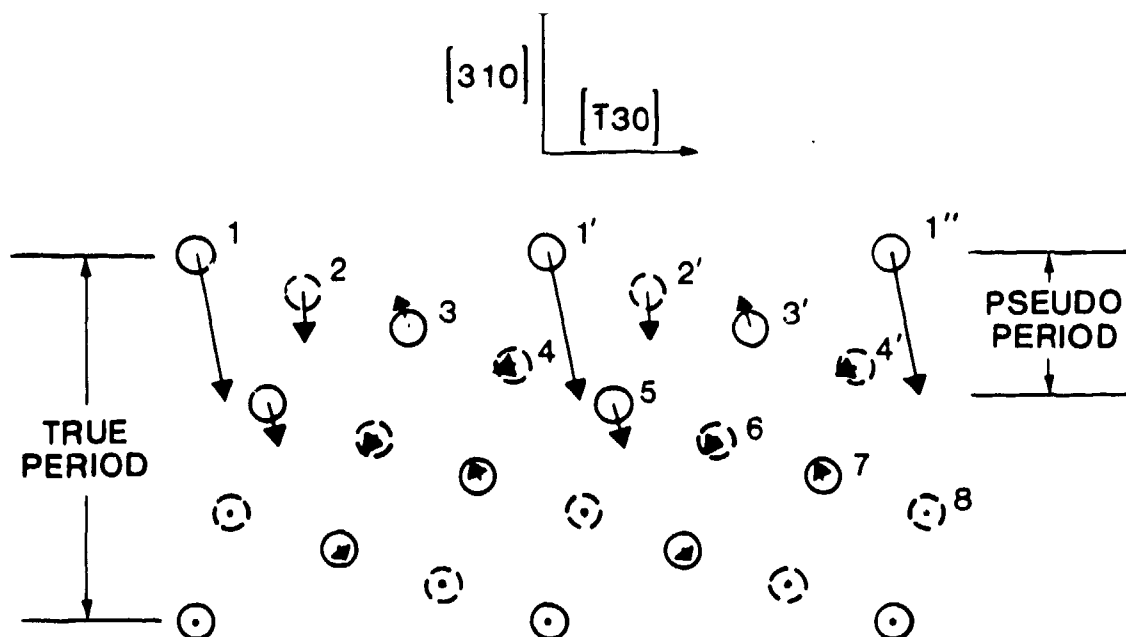


Figure 2. Relaxation of the Ni (310) surface. The circles represent unrelaxed atomic positions (dotted atoms lie $a_0/2$ below the other atoms). The vectors show the relaxation motion of the atoms, magnified 20 times.

steric interactions between the atoms, the length of this pseudo-period must be less than or equal to the nearest neighbor distance. The equality only holds for the highest symmetry surfaces in which the outermost atom pushes directly down on the atom below with no lateral component of force (i.e. on the (110) surface in FCC materials). As the index of the surface increases, the lateral forces on the atoms below the first period increase. In some cases, these lateral forces dominate those perpendicular to the surface and, in these cases, the simple picture of a completely periodic surface relaxation is no longer strictly applicable (see the (410) and (520) surfaces of Al in Fig. 1).

This simple picture of the outermost atoms pushing inward and the more deeply buried atoms responding sterically may be used to account for a number of the other features of surface relaxation. Since the pseudo-period in the direction perpendicular to the surface is directly related to the period in the surface (see Fig. 2), it is not surprising that surfaces with two steps per period (along the surface) have twice the number of oscillations per period than those with only one step (i.e. two major points in each period which are pushing down instead of one). This explains why the surface relaxation oscillates twice as fast for the (320) and (520) surfaces compared with the (110), (210), (310), and (410) surfaces (see Fig. 1). The amplitudes of the oscillations appear to decay exponentially with depth into the bulk. Such a decay may be understood in terms of an elastic half-space which is subjected to normal force along parallel lines on the surface[9]. These parallel lines correspond to the outermost atoms on the steps of the surface and the pressure corresponds to the inward relaxation of those atoms. The resultant strain in the bulk scales decays as $\alpha z e^{-\beta z}$ for large z , where α and β are constants and z measures distance into the bulk.

Given that surface relaxations are periodic and decay as $z e^{-\beta z}$, we propose a generic form for surface relaxation

$$\Delta d(z) = A z e^{-Bz} \text{Mod}(z, \lambda) \quad (1)$$

where A and B are constants and $\text{Mod}(z, \lambda)$ indicates a periodic function of z with wave-length λ . As long as the index of the surface is not too high, the

geometry of the surface (see Fig. 2). The constant α is expected to vary from surface to surface and metal to metal. Like the Mod function, we expect that B will be determined by the geometry of the surface.

NiAl AND Ni₃Al SURFACE RELAXATIONS

Many of the features of surface relaxations in pure metals are also found in order alloys. However, additional features appear which are entirely due to the nature of the ordered nature of these materials. For example, the (111) and (100) surfaces of NiAl may terminate as either pure Ni or pure Al. While each plane parallel to the NiAl (110) surface has the same composition, the atomic planes may ripple. In Table II we show the results of our simulation of NiAl(110) and a comparison with existing LEED data. The data in this case is reported in terms of the $\Delta d_{n,n+1}$ measured between the Ni atoms on each plane and R_n , which is the amount by which layer n is rippled (Al out, Ni in corresponds to positive R_n), normalized by the interplanar spacing. As in the pure metals the surface relaxation is oscillatory and the amplitude of the relaxation decays rapidly (however, the decay is slow compared to that in pure Ni and Al). While in the pure metals the outermost layer always relaxes inward, on this surface we find that the Al atoms move out and the Ni atoms move in. This rippling of the atomic planes continues deep into the bulk, with the sign of the rippling alternating layer by layer. While this is in agreement with the experimental data [10], the absolute magnitude of the relaxation is not in very good agreement. However, since the LEED data¹¹ was analyzed assuming that only atom layers 1 and 2 are displaced, the actual disagreement may not be as bad as is indicated.

TABLE II. Surface relaxations on the NiAl (110) from the simulations and LEED data.

n	$\Delta d_{n,n+1}$ (%)		R_n (%)	
	Simulation	LEED [10]	Simulation	LEED [10]
1	-12.48	-4.6	+16.19	+9.8
2	+11.80	+1.0	-11.74	+1.0
3	-6.88	.	+8.19	.
4	+5.26	.	-5.65	.
5	-3.07	.	+3.61	.
6	+1.84	.	-2.22	.

The NiAl (100) and (111) surfaces and the atomic layers parallel to them are made up of either all Ni or Al and hence no rippling occurs. In both cases we find that the Al terminated surfaces are lower in energy than the Ni terminated surfaces. While the Ni terminated (100) surface is higher in energy by 167 mJ/m² than the Al terminated surface (1752 mJ/m²), we find that the Ni terminated (111) surface is only 29 mJ/m² higher in energy than the Al terminated surface (1900 mJ/m²). Since these surfaces are currently under experimental investigation, we report data on both possible terminations (Table III). Again we see the same type of oscillatory, rapidly decaying surface relaxations discussed above. It is interesting to note that for NiAl (111), the Al terminated surfaces relax outward, while the Ni terminated surfaces relax inward.

While we have performed similar surface relaxation simulations for Ni₃Al, due to the complicated nature of the crystal structure and space limitations we must refer the interested reader to Ref. 11. The three Ni₃Al surfaces studied all showed damped, oscillatory relaxations. In Ni₃Al the (110)

$\Delta d_{n,n+1}$	(100)		(111)	
	Ni Termination	Al Termination	Ni Termination	Al Termination
$\Delta d_{1,2}$	+0.273	+5.625	-16.998	+6.479
$\Delta d_{2,3}$	+1.109	+0.765	+3.139	-8.542
$\Delta d_{3,4}$	-0.614	+0.025	+8.108	+4.769
$\Delta d_{4,5}$	-0.017	-0.162	-5.788	+2.248
$\Delta d_{5,6}$	+0.004	-0.117	+0.722	-4.524

and (100) surfaces may be terminated either with only Ni atoms or with an equal atomic mixture of Ni and Al. For the (100) surface we find that the mixed termination is approximately 1% lower in energy, while for the (110) surface the pure Ni termination is approximately 1.5% lower in energy. These deviations are near the limit of reliability of the potentials and in the (110) case contradict the only piece of experimental data[12]. In all cases, we find that the planes containing both Ni and Al are rippled as found above in NiAl.

Both the generally observed phenomena of the outward relaxation of the Al atoms on the surface as well as the propensity toward Al or Al rich surface terminations may be understood by considering the relative sizes of the Ni and Al atoms. In pure metals, surfaces generally contract as the atoms move in to increase the local density toward their bulk value. However, in Ni_3Al and NiAl, the Al atoms are under compression due to the fact they are larger than the Ni atoms. (The lattice parameter of Ni_3Al is very close to that of pure Ni such that the Al atoms suffer a 12% contraction.) Therefore, the Al atoms at the surface tend to move out to decrease the density and achieve a less stressed state. Since the Al atoms are under much greater compression than the Ni atoms are under tension, a greater amount of strain energy is relieved by terminating the crystal with an Al or Al rich surface.

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